

# EQUATION OF STATE OF POLYMER LIQUIDS\*

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## I. Introduction

In a series of recent papers<sup>1-5</sup> we have discussed the equation of state, cohesive energy density (c.e.d.) and the internal pressure ( $p_i$ ) of oligomer liquids and amorphous polymers of widely differing structures at atmospheric and elevated pressures. The discussion was based on two alternative approaches, namely statistical mechanics, specifically a partition function based on cell theory and thermodynamics, i.e. a principle of corresponding states (PCS). The validity of the latter over the whole range of volumes and pressures experimentally available could be established. The cell theory is consistent, of course, with the PCS, but yields correct thermal expansivities and c.e.d.'s for reduced volumes  $\tilde{V}$  between about 1 and 1.2 only, deviating systematically for  $\tilde{V} > 1.2$ . The internal pressure-volume function shows a maximum in the range in which the reduced experimental function is monotonic.

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This discrepancy clearly reflects the defect of the theory in respect to entropy.

Most recently<sup>5</sup> we have explored the effect of lattice vacancies or holes in the quasilattice. Previous efforts in this direction<sup>6</sup> had been restricted to fluids with spherical force fields. The new features introduced in the partition function by the presence of holes are a) a volume dependent combinatory factor, b) a lattice energy which depends on the fraction  $y$  of occupied sites, and c) a cell partition function which varies with  $y$ . The purpose of the present paper is to discuss particular forms of this latter dependence and to compare the resulting equation of state and other quantities with experiment. In this we shall limit ourselves to essentially atmospheric pressure data.

## II. Recapitulation of Cell Theory Results

Assuming a square well cell potential and a 6-12 potential between segment pairs, we have for the configurational partition function:

$$Z = (v^{1/3} - 2^{-1/6} v^{*1/3})^{3cN} \exp\left\{-Nqz\epsilon^*/(2kT)[1.011(v^*/v)^4 - 2.409(v^*/v)^2]\right\} \quad (1)$$

Here  $v$  is the volume per chain segment,  $v^*$  the corresponding characteristic volume defined in terms of the pair potential and the lattice geometry,  $\epsilon^*$  the potential minimum,  $qz = s(z - 2) + 2$  the number of nearest neighbors of an  $s$ -mer, and the numerical constants are those corresponding to a face centered cubic lattice. The parameter  $3c$  is the number of external degrees of freedom, with  $\lim_{s \rightarrow \infty} c/s = \text{const.}$  From (1) one obtains

6) See, for example, H. Eyring, D. Henderson, B. J. Stover and E. M. Eyring, "Statistical Mechanics and Dynamics", John Wiley and Sons, New York, 1964, p. 376.

a principle of corresponding states in terms of the following reduced variables:

$$\begin{aligned}\tilde{V} &= V/V^* = v/v^*; \quad \tilde{T} = T/T^* = ckT/(qz\epsilon^*); \\ \tilde{p} &= p/p^* = pV^*/(qz\epsilon^*)\end{aligned}\quad (2)$$

and the results:

$$\frac{\tilde{V}}{\tilde{p}\tilde{T}} = (1 - 2^{-1/6}\tilde{V}^{-1/3})^{-1} + 2/(\tilde{T}\tilde{V}^2)(1.011\tilde{V}^{-2} - 1.2045) \quad (3)$$

$$c.\tilde{e}.d. = 1/(2\tilde{V}^3)(2.409 - 1.011\tilde{V}^{-2}) \quad (4)$$

$$\tilde{p}_i = (2/\tilde{V}^3)(1.2045 - 1.011\tilde{V}^{-2}) \quad (5)$$

These expressions have been compared earlier with the experimental "master" curves which verify the validity of PCS and analytical expressions for the latter have been obtained.<sup>1-5</sup> All comparisons between theory and experiment are then based on these master curves.

### III. Hole Theory

For the volume dependent part of Z we now write in place of eq. (1):

$$Z = g \cdot Q^N \exp(-E_0/kT) \quad (1a)$$

with  $Q = f^{3c}$  and  $f$  the cell partition per degree of freedom of the chain.

For the computation of the combinatorial factor  $g$  we select a lattice consisting of  $Ls$  sites on which are placed the  $Ns$  segments of the  $N$  chains with  $N \leq L$ , and assume equal sizes of segments and holes. This yields:<sup>5</sup>

$$g = (Ns + N_h)^{N+N_h} / (N_h^{N_h} \cdot N^N) \quad (6)$$

with  $N_h = (L - N)s$  the number of unoccupied lattice sites. The reduced lattice energy per molecule now becomes:

$$\tilde{E}_0 = (y/2)[1.011(v^*/\omega)^4 - 2.409(v^*/\omega)^2] \quad (7)$$

where  $y = N/L$  and  $\omega = yv$  represents the volume of a cell or the volume

per site. It should be noted at this point that the fraction of occupied sites  $y$  is a function of both  $T$  and  $V$  (see below) and hence  $E_0$  and  $Q$  are no longer functions of volume solely as in the absence of lattice vacancies, eq. (1).

From eqs. (1a), (6), and (7) we obtain for the configurational Helmholtz free energy:<sup>5</sup>

$$F/N = kT[\ln(y/s) + s(1-y)\ln(1-y)/y] - 3ckT \ln f + (qze^*y/2)[1.011(y\tilde{V})^{-4} - 2.409(y\tilde{V})^{-2}] \quad (8)$$

The cell size or fraction  $y$  at equilibrium minimizes the free energy or

$$(\partial F/\partial y)_{V,T} = 0$$

yielding the condition for  $y$ :

$$(s/3c)[(s-1)/s + \ln(1-y)/y] = -y(\partial \ln f/\partial y)_{V,T} + [y/(6\tilde{T})]/(y\tilde{V})^2 \cdot [2.409 - 3.033/(y\tilde{V})^2] \quad (9)$$

Recalling in view of the extremum condition that

$$p = -(\partial F/\partial V)_T = (\partial F/\partial y)_{T,\omega} y/V$$

we obtain<sup>5</sup>

$$\frac{p\tilde{V}}{\tilde{T}} = 3y[(\partial \ln f/\partial y)_{V,T} - (\partial \ln f/\partial y)_{\omega,T}] + (2y/\tilde{T})/(y\tilde{V})^2 [1.011/(y\tilde{V})^2 - 1.2045] \quad (3a)$$

Eq. (3a) together with the solution of eq. (9) for  $y$  determines the equation of state. As we have remarked earlier,<sup>5</sup> eq. (9) is strictly compatible with the principle of corresponding states only provided the ratio  $s/c$  assumes a universal value. Our earlier results certainly show wide variations of this ratio with the nature of the substituents and the chain backbone.<sup>1,2</sup> Yet, it will turn out that the results are within wide limits practically independent of the specific value assigned to the

quantity  $c/s$ . There is moreover, an apparent dependence on molecular weight through the factor  $(s - 1)/s$  which varies between zero and unity. However, a similar insensitivity of the results may be anticipated.

In order to proceed further, we must specify the dependence of  $f$  on  $y$  and the variables of state. In earlier free volume theories for spherical molecules a linear dependence of the logarithm of the free volume on the number of holes was assumed.<sup>6</sup> Recently Henderson<sup>7</sup> achieved a notable improvement by postulating a linear relation involving the free volume itself. In his theory the free volume is averaged over a "gas" and a "solid"-like free volume with weight factors  $(1 - y)$  and  $y$  respectively. In our notation and generalized for our systems, this implies the relationship:

$$f = [y(\omega^{1/3} - 2^{-1/6}v^{*1/3})^3 + (1 - y)\omega]^{1/3} \quad (10a)$$

Alternatively, we may average the cell partition function per degree of freedom, thus:

$$f = y(\omega^{1/3} - 2^{-1/6}v^{*1/3}) + (1-y)\omega^{1/3} = \omega^{1/3} - 2^{-1/6}v^{*1/3}y \quad (10b)$$

Preliminary calculations of the various thermodynamic quantities indicate qualitatively similar results based on eqs. (10a) and (10b) respectively. However, the linear relation (10b) appears to yield a superior quantitative agreement with experiment. Hence, we shall now explore the consequences of eq. (10b) in detail.

Substitution of eq. (10b) into (9) and (3a) yields the determining equation for  $y$ , viz.:

$$\begin{aligned} (s/(3c)[(s-1)/s + \ln(1-y)/y] = (2/3-X)/X \\ + [y/6T]/(yV)^2 [2.409 - 3.033/(yV)^2] \end{aligned} \quad (9a)$$

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7) J. Henderson, J. Chem. Phys., 37, 631 (1962).

and the equation of state:

$$\frac{p\tilde{V}}{T} = 1/X + (2y/\tilde{T})/(y\tilde{V})[1.011/(y\tilde{V})^2 - 1.2045] \quad (3b)$$

$$\text{with } X = 1 - 2^{-1/6} y/(y\tilde{V})^{1/3}$$

For long chains and at atmospheric (zero) pressure, eq. (9a) reduces to:

$$\begin{aligned} (s/3c)[1 + \ln(1 - y)/y] &= (2/3 - X)/X \\ +1/(12X) \cdot [2.409 - 3.033/(y\tilde{V})^2] &/[1.2045 - 1.011/(y\tilde{V})^2] \end{aligned} \quad (9b)$$

Table I shows  $y$  as a function of  $\tilde{V}$  at atmospheric pressure and assuming  $s/(3c) = 1$ , the value appropriate for an  $s$ -mer with freely rotating segments and no side group motions. We note the initial slow decrease of  $y$  with increasing  $\tilde{V}$  and the subsequent relative constancy of the reduced cell size  $\tilde{\omega} = y\tilde{V}$  with increasing volume.

Table I

Equilibrium Fraction  $y$  of Occupied Sites, eq. (9b) as a Function of Reduced Volume at Atmospheric Pressure

$\tilde{V}$	$y$	$y\tilde{V}$
0.9415	0.9999	0.9414
0.9480	0.9983	0.9464
0.95	0.9972	0.9473
0.96	0.9897	0.9501
1.00	0.9536	0.9536
1.05	0.9101	0.9556
1.10	0.8703	0.9573
1.15	0.8339	0.9590
1.20	0.8006	0.9607
1.25	0.7699	0.9624
1.30	0.7416	0.9641
1.35	0.7155	0.9659
1.40	0.6912	0.9677
1.45	0.6687	0.9696
1.50	0.6476	0.9714

We can now construct the zero pressure isobar by substituting the appropriate values from Table I into eq. (3b) with the left hand side equal to zero. Fig. 1 exhibits a comparison between the  $\tilde{V} - \tilde{T}$  curve so calculated, the earlier result of the cell theory, eq. (3), and the experimental master curve.<sup>2</sup> Since eqs. (3) and (3b) define two different systems of coordinates, it is necessary to shift, for example, the cell model and the experimental curve along both axes. The connection between the former and the hole theory is made by the equations:

$$\log [\tilde{V}(\text{cell})/\tilde{V}(\text{hole})] = 0.023; \log [\tilde{T}(\text{cell})/\tilde{T}(\text{hole})] = 0.395 \quad (11)$$

It appears from the results of Fig. 1 that the theory, with the assumed value of  $s/c$  describes very satisfactorily the observed reduced volume-temperature relation at atmospheric pressure, except perhaps for the very last portion,  $\tilde{V}_{\text{cell}} > 1.45 = 1.38 \times 1.0544$  in contrast to the result of the simple cell theory. We have convinced ourselves that a value of  $s/(3c) = 0.3$ , leads to practically the same curve with, of course, a different system of reduced variables. It should be noted in this connection that the values of  $s/(3c)$  derived in terms of the cell theory coordinates<sup>1,2</sup> vary between about 0.6 for polymethylene and 0.06 for polystyrene.\*

From eq. (8), the relation  $U = -T^2[\partial(F/T)/\partial T]_V$  and eq. (9) we derive:

$$c.e.d. = (y/2\tilde{V})/(\tilde{y}\tilde{V})^2[2.409 - 1.011/(\tilde{y}\tilde{V})^2] \quad (4a)$$

Fig. 2 presents a comparison with the cell theory and the experimental (PCS) result.<sup>2,5</sup> In order to obtain the transformation factor for the reducing pressure  $p^*$ , eq. (2), we make use of the fact, that the cal-

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\* It must be recalled that for the actual  $n$ -mer  $s < n$ , because of the assumption of a uniform quasilattice.

culated values of the c.e.d. must become identical in both theories as  $y \rightarrow 1$ . By graphical extrapolation we observe that  $\lim(y\hat{V}) = 0.94$  and deduce from eqs. (4), (11) and (4a)

$$p^*(\text{hole})/p^*(\text{cell}) = 0.9306 \quad (11a)$$

when  $s/(3c) = 1$ .

It must be admitted that in the region in which the two theories begin to depart from each other, the cell theory gives somewhat smaller deviations from experiment. Once more, a change in the numerical value of  $s/c$  is inconsequential for the shape of the theoretical curve.

Finally, we obtain the internal pressure from the definition

$$p_i = (\partial U / \partial V)_T = (\partial U / \partial V)_{T,y} + (\partial U / \partial y)_{T,V} (\partial y / \partial V)_T$$

with the result:

$$p_i = (1/2)/(y\hat{V})^2 [2.409 - 3.033/(y\hat{V})^2] (\partial y / \partial \hat{V})_T + (2y/\hat{V})/(y\hat{V})^2 [1.2045 - 1.011/(y\hat{V})^2] \quad (5a)$$

The derivative follows from the minimization condition. Writing eq. (9b)

in the form  $\phi(y, \hat{V}, \hat{T}) = 0$ , we have

$$(\partial y / \partial \hat{V})_{\hat{T}} = -(\partial \phi / \partial \hat{V})_{y, \hat{T}} / (\partial \phi / \partial y)_{\hat{V}, \hat{T}}$$

and finally

$$(\partial y / \partial V)_{\hat{T}} = (y/\hat{V}) \{ 2(1-x)(3x^2) - (y/2\hat{T}) / (y\hat{V})^2 [12.132/(y\hat{V})^2 - 4.818] \} x \{ 4(1-x)/(3x^2) + (y/2\hat{T}) / (y\hat{V})^2 [9.099/(y\hat{V})^2 - 2.409] + (s/cy) \ln(1-y) + s/[c(1-y)] \}^{-1} \quad (12)$$

Fig. 3 shows eqs. (5) and (5a) with  $s/(3c) = 1$ , compared with the experimental (PCS) result. Although numerical agreement is still lacking, an improvement over the cell theory is noticeable. The new curve is monotonic over the range of volumes encountered experimentally. Also it is convex to the  $\hat{V}$ -axis. A change in the value of  $s/(3c)$  to 0.3 raises



the low temperature part of the curve somewhat, but does not suffice to improve the agreement significantly.

#### IV. Conclusions

The extra entropy resulting from the introduction of lattice vacancies, together with the relation (10b) for the cell partition function, leads to a significant improvement in the reduced volume-temperature function at atmospheric pressure. No improvement is observed in respect to the c.e.d. As for the internal pressure function, the numerical agreement is still not sufficient. In the present theory, the lattice picture has been used additionally to evaluate the combinatorial factor  $g$ , eq. (6), in the partition function (1a). Moreover, equal sizes of holes and chain segments are assumed. The use of this equation may contribute to the relative inadequacy of the derivative  $(\partial S/\partial V)_T$ , in contrast to the behavior of the function  $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$ . Finally, we observe that in the expression for the configurational heat capacity

$$\tilde{c}_v = (\partial \tilde{U}/\partial \tilde{T})_{\tilde{V}, \tilde{y}} + (\partial \tilde{U}/\partial \tilde{y})_{\tilde{T}, \tilde{V}} (\partial \tilde{y}/\partial \tilde{T})_{\tilde{V}}$$

the first term vanishes in the square well approximation for the cell potential, as in the unmodified theory, but the second makes a positive contribution, as it should.

LEGENDS FOR FIGURES

Fig. 1. Comparison between experimental (the points) and theoretical reduced isobars at atmospheric pressure. Full line, hole theory, eqs. (3b) and (9b); dashed line, cell theory, eq. (3).

Fig. 2. Comparison between experimental (the points) and theoretical reduced cohesive energy densities at atmospheric pressure. Full line, hole theory, eqs. (4a) and (9b); dashed line, cell theory, eq. (4).

Fig. 3. Comparison between experimental (the points) and theoretical reduced internal pressures computed at atmospheric pressure. Full line, hole theory, eqs. (5a) and (9b); dashed line, cell theory, eq. (5).

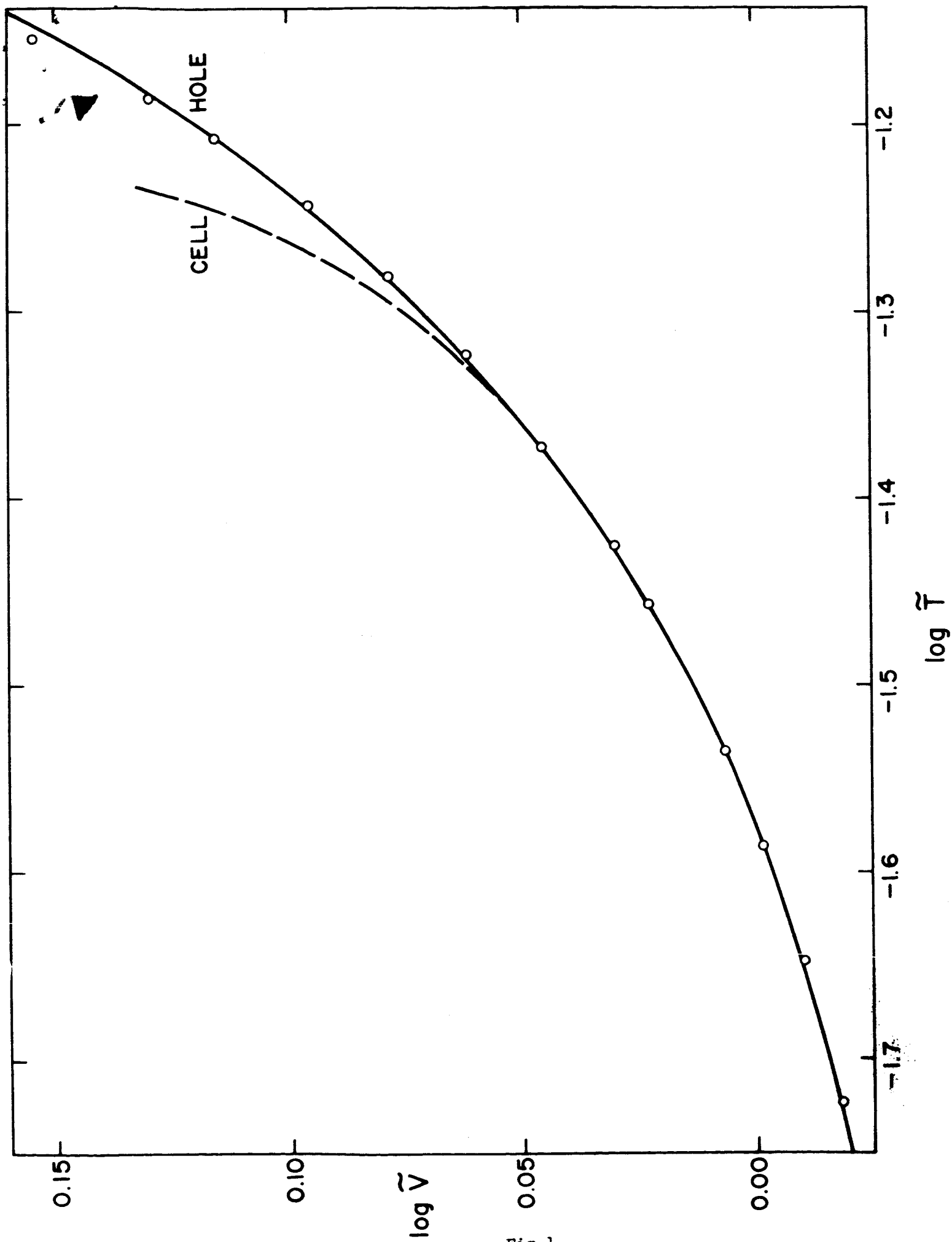


Fig.1

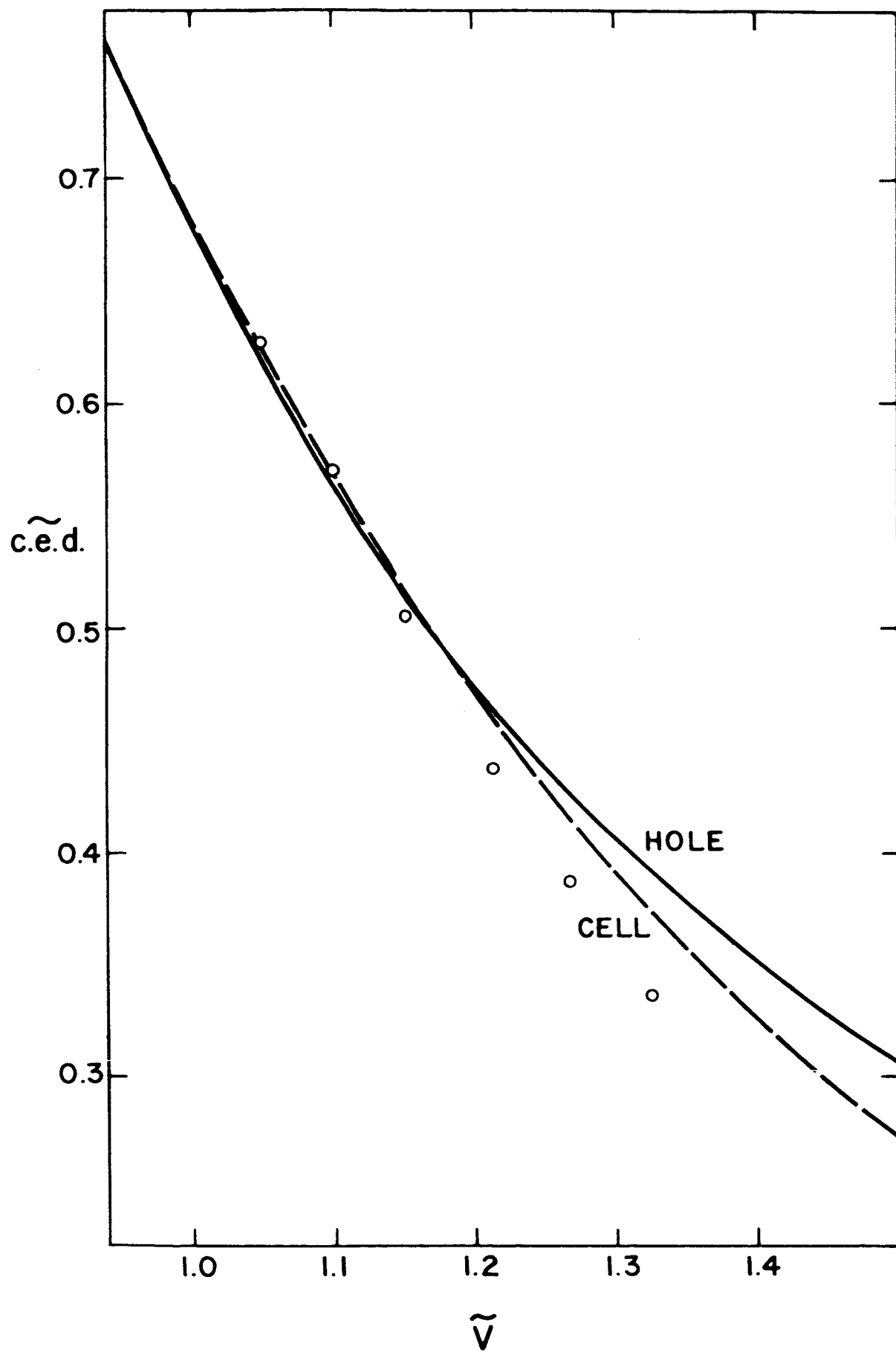


Fig.2

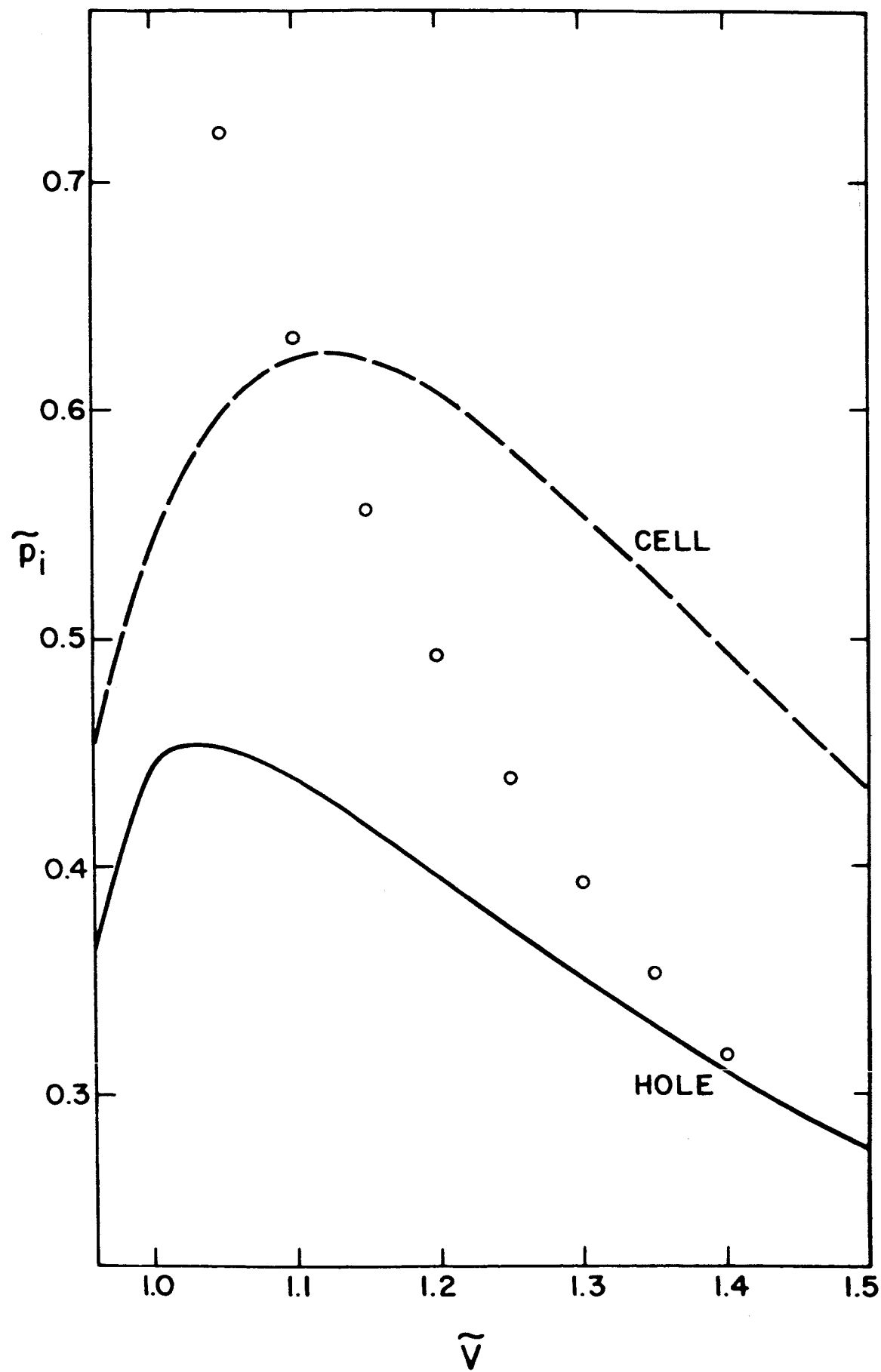


Fig.3